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Semiclassical description of purely rotational recurrences for collisionless asymmetric top molecules: new results

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Abstract

A semiclassical approach, based on the discrete WKB approximation, is developed for the description of purely rotational recurrences in thermal ensembles of collisionless asymmetric top molecules. Exact non-perturbative expressions are derived for the periods of the J-, H-, and K-type transients. These formulas automatically account for the phenomenon of increasing the period of the J-type transients for oblate asymmetric tops and decreasing that for prolate asymmetric tops in parallel with the enhancement of molecular asymmetry. The asymmetry corrections are demonstrated to magnify the period of the K- and H-type transients, irrespective of the form of the molecular top. The polarity of the A- and C-type transients is established. New kinds of transients are predicted and characterized by their periods and polarity. The most important of these is demonstrated to be the P-type transients arising for planar molecules. © 2000 Published by Elsevier Science B.V. All rights reserved.

PACS: 03.65.Sq; 42.50.Md

1. Introduction

Several dozens of years ago, both experimental [1] and theoretical (see e.g. Ref. [2]) indications were obtained that the rotational rephasing effects in thermal ensembles of molecular species should manifest themselves in the polarization sensitive time domain measurements. The first observations of rotational recurrences (RRs) in the collisionless ensembles of *trans*-stilbene, *trans*-stilbene-d$_{12}$ and *trans*-stilbene–Ar complexes under the cooling in the supersonic jet were reported in Refs. [3,4]. Since that time, the rotational coherence spectroscopy (RCS) has been developed into a powerful technique for determining the main moments of inertia of polyatomic molecules, structures of van der Waals complexes of polyatomic molecules and various species, and also for defining directions of absorption and emission dipole moments in the molecular frame [5]. Refs. [6–12] and the literature cited therein give an account of the recent experimental progress in the field of RCS.

A theoretical basis for the RCS has been developed in papers [13–18]. More specifically, a polarization response of an ensemble of molecules under collision-free conditions is proportional to the quantum orientational correlation function (OCF) of the dipole moments involved

$$r^\lambda(t) \sim \langle P^\lambda(\hat{\vec{\mu}}_1(0)\hat{\vec{\mu}}_2(t))\rangle. \tag{1}$$

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The time dependence here is entirely due to the free rotation of molecules; $\langle \cdots \rangle$ denotes the quantum mechanical averaging over the initial states and summation over the final states; $\vec{\mu}_1$ and $\vec{\mu}_2$ stand for the pump–probe or absorption–emission dipole moments; $P^\lambda(x)$ is the Legendre polynomial of the rank λ, and caps are used to designate operators. There exists no problem to write down the explicit analytical expression for this OCF in the case of symmetric top molecules [13–15]. Such an equation allows one to classify all the possible kinds of transients in the collisionless ensemble of symmetric tops to determine the polarity of the transients and also to derive extremely simple analytical formulas that express the transient periods through the rotational constants of the molecules [13–16]. The case of asymmetric tops is more involved. Indeed, a direct computation of asymmetric top quantum OCFs presents no difficulties [15–18]. These OCFs depend on temperature (which is a few kelvins for experiments in supersonic jets), rotational constants and directions of dipole moments in the molecular frame. By varying the two latter sets of parameters, one can try to bring into correspondence the calculated and experimental transients, thereby getting knowledge on the rotational constants and directions of the dipole moments. This is the standard approach to the interpretation of measured RRs [3–18]. However, this procedure is essentially numerical, and it hardly allows one to grasp general tendencies in the variation of the RR periods vs. molecular parameters. Before embarking on performing experiments on specific molecules and/or complexes, it would be desirable to have guidelines on possible kinds, periods, and polarity of the transients.

If the asymmetric molecule under study can roughly be considered as a prolate or oblate symmetric top, one would expect that the RR periods would be described fairly well by (slightly modified) formulas derived for the pertinent symmetric tops. It has been proved, that such formulas work surprisingly well [3–18]. Moreover, the new kinds of asymmetry transients (the so-called C- and A-type transients) were established and characterized by invoking semiclassical treatment of the asymmetric top rotation [18]. In addition, one can get valuable insight into the problem of

the RRs by considering the classical mechanics symmetric [13–16] and asymmetric [19–21] top OCFs, but with the rotational frequencies replaced by their quantum (discrete) analogues.

It is the aim of the present work to carry out a comprehensive semiclassical study of the RRs in the ensemble of collisionless asymmetric top molecules. Following this way, it is possible to perform a complete and uniform analysis and classification of the RRs for asymmetric tops, to derive accurate non-perturbative expressions for the RR periods, and also to predict new kinds of transients. The outline of the paper is as follows: General formulas for quantum asymmetric top OCFs of an arbitrary rank are introduced in Section 2. A semiclassical analysis of the OCFs is made in Section 3. The results of this analysis are discussed in Section 4. Our main findings and conclusions are briefly summarized in Section 5.

2. Asymmetric top orientational correlation functions

Let

$$\hat{H} = A\hat{L}_x^2 + B\hat{L}_y^2 + C\hat{L}_z^2 \tag{2}$$

be the asymmetric top Hamiltonian. Here $\hat{L}_i$ are the angular momentum operators in the molecular frame and $A = \hbar^2/2I_A$, $B = \hbar^2/2I_B$, $C = \hbar^2/2I_C$ are the rotational constants. Without loss of generality, we shall further assume that the main moments of inertia are arranged according to the requirement $I_C \geqslant I_B \geqslant I_A$, so that $A \geqslant B \geqslant C$. In the Heisenberg representation, Eq. (1) looks like the following:

$$\langle P^\lambda(\hat{\vec{\mu}}_1(0)\hat{\vec{\mu}}_2(t)) \rangle = Z^{-1} \, \mathrm{Sp}\left(\sum_{a=-\lambda}^{\lambda} \exp\{-\hat{H}/kT\} D_{0a}^\lambda(-\vec{\mu}_1) \right.$$
$$\left. \times \exp\{-it\hat{H}/\hbar\} D_{a0}^\lambda(\vec{\mu}_2) \exp\{it\hat{H}/\hbar\} \right). \tag{3}$$

Here, the partition function

$$Z = \mathrm{Sp}\left(\exp\{-\hat{H}/kT\} \right) \tag{4}$$

and $D_{a0}^\lambda(\vec{\mu})$ are the Wigner functions. To get the explicit form of Eq. (3), it is convenient to rewrite

it in the basis of the symmetric top eigenfunctions $|J, K, M\rangle$. Here, the standard quantum notation is used: $J(J + 1)$ is the eigenvalue of the square of the angular momentum, K and M are, respectively, the eigenvalues of the projection of the angular momentum on the z-axis of the molecular and laboratory frame. It is further convenient to introduce the quantity $\Xi_{K_1 K_2}^J(x)$ according to the definition,

$$\langle J_1 K_1 M_1 | \exp\{x\hat{H}\} | J_2 K_2 M_2 \rangle$$
$$\equiv \delta_{J_1 J_2} \delta_{M_1 M_2} \Xi_{K_1 K_2}^{J_1}(x) \tag{5}$$

(x is an arbitrary number). Explicitly,

$$\Xi_{K_1 K_2}^J(x) \equiv [\exp\{xH^J\}]_{K_1 K_2}, \tag{6}$$

where $\langle J_1 K_1 M_1 | \hat{H} | J_2 K_2 M_2 \rangle \equiv \delta_{J_1 J_2} \delta_{M_1 M_2} H_{K_1 K_2}^J$, and $H_{K_1 K_2}^J$ is regarded as a matrix with the elements

$$\begin{aligned}
H_{KK}^J &= \{(A + B)[J(J + 1) - K^2] + 2CK^2\}/2 \\
&\equiv G^J(K), \\
H_{KK+2}^J &= (A - B)\sqrt{(J + K + 2)(J + K + 1)} \\
&\quad \times \sqrt{(J - K - 1)(J - K)}/4 \\
&\equiv V^J(K).
\end{aligned} \tag{7}$$

While writing down formulas (7), the explicit assumption was made that the axis C of the smallest moment of inertia was used as the quantization axis. By cyclic permutation of rotational constants A, B, and C, one can readily obtain analogous expressions in the case of A and B quantization axes. In terms of quantities (6), one arrives at the expressions,

$$\langle P^\lambda(\hat{\vec{\mu}}_1(0)\hat{\vec{\mu}}_2(t)) \rangle = \sum_{a,b=\lambda}^{\lambda} D_{(0a)}^\lambda(-\vec{\mu}_1) F_{ab}^\lambda(t) D_{b0}^\lambda(\vec{\mu}_2), \tag{8}$$

$$\begin{aligned}
F_{ab}^\lambda(t) &= Z^{-1} \sum_{J,J'=0}^{\infty} \sum_{\substack{K_1,K_2, \\ K_3,K_4}} (2J + 1) C_{JK_2,\lambda a}^{J'K_3} C_{JK_1,\lambda b}^{J'K_4} \Xi_{K_1,K_2}^J \\
&\quad \times (1/kT) \Xi_{K_2,K_3}^{J'}(\mathrm{i}t/\hbar) \Xi_{K_3,K_4}^{J}(-\mathrm{i}t/\hbar).
\end{aligned} \tag{9}$$

Here, $C_{J_1 K_1 J_2 K_2}^{JK}$ are the Clebsch–Gordan coefficients. The summation in Eq. (9) is expanded over those values of indexes, for which the

Clebsch–Gordan coefficients are non-zero. In particular, the selection rules

$$|J - J'| \leqslant \lambda, \quad K_3 = K_2 + a, \quad K_4 = K_1 + b \tag{10}$$

must be obeyed. Eq. (9) explicitly defines the asymmetric top OCF, which is the fundamental quantity for the subsequent analyses, since it contains all the dynamic information on the molecular rotation. Our basic expressions (8) and (9) are very similar to that given in Section 3 of paper [17]. The only difference stems from the fact that the explicit form of equations like Eqs. (1) and (3) is given in Ref. [17] in terms of the eigenfunctions of the asymmetric top Hamiltonian, that are linear combinations of functions $|J, K, M\rangle$.

If the molecule under consideration is a symmetric top $(A = B)$, then all the Ξ matrices entering Eq. (9) are diagonal,

$$\begin{aligned}
\Xi_{K_1 K_2}^J(x) &= \Xi_{K_1 K_1}^J(x)\delta_{K_1 K_2} \\
&\equiv \exp\{xH_{K_1 K_1}^J\}\delta_{K_1 K_2},
\end{aligned} \tag{11}$$

so that the Eq. (9) simplifies to the well-known symmetric top OCF [13–16]. For asymmetric top molecules, one can also employ the secular (symmetric top like) approximation,

$$\Xi_{K_1 K_2}^J(x) \approx \exp\{xH_{K_1 K_1}^J\}\delta_{K_1 K_2}. \tag{12}$$

This is equivalent to the complete neglecting by all the off-diagonal elements of matrix $H_{K_1 K_2}^J$. Despite the fact that this approximation is somewhat uncontrolled and unjustified, it leads to surprisingly accurate expressions for the RR periods (see papers [3–21] and discussion given below).

3. Semiclassical approximation

For an asymmetric top molecule, one can write

$$\Xi_{K_1, K_2}^J(x) = \sum_{N=-J}^{J} f_{K_1 N}^J \exp\{-xE(J, N)\} f_{NK_2}^J, \tag{13}$$

where $E(J, N)$ and f_{KN}^J are the eigenvalues and eigenfunctions of three-diagonal matrix $H_{K_1 K_2}^J$. (Note that the quantities f_{KN}^J are nothing else than the coefficients in the linear expansion of the asymmetric top eigenfunctions over the symmetric top

ones.) It is quite simple and straightforward to find $E(J, N)$ and f_{KN}^J numerically, that allows one to calculate OCF (9). A very similar procedure was carried out in Refs. [15,17].

However, one can get a deeper insight into the problem by applying the semiclassical approximation. The criterion of the validity of semiclassical description of molecular rotation can immediately be established by considering the ratio ε of the rotational and thermal energy. If I is a characteristic moment of inertia of a polyatomic molecule ($I \sim 10^3$–10^4 a.u. Å^2), one finds the ratio $\varepsilon = \hbar^2/2IkT \ll 1$, even under the conditions of supersonic cooling ($T \sim 5$ K). In this case, high enough values of the angular momentum contribute significantly to the summation in Eq. (9). The semiclassical approach was successfully invoked for the calculation of the eigenvalues and eigenfunctions of the rigid asymmetric top Hamiltonian [22–27]. However, the technique has not been applied to the analyses of quantum asymmetric top OCFs. For these purposes, it is ideally suited to the discrete WKB method developed by Braun [28,29] (the state of the art of the theory was recently reviewed in Ref. [30]). Indeed, by invoking the explicit form of matrix $H_{K_1 K_2}^J$, the problem of finding its eigenvalues and eigenfunctions reduces to the solution of the three-term recurrence relations

$$V^J(K-2)f_{K-2N}^J + [G^J(K) - E(N, J)]f_{KN}^J$$
$$+ V^J(K)f_{K+2N}^J = 0. \tag{14}$$

This task has been solved by Braun and Kiselev [30–32] (see also Refs. [22,23,33,34]), so we present

here all the necessary results for granted. All the possible values of the asymmetric top rotational energy are limited by the inequality

$$Cj^2 < E < Aj^2 \tag{15}$$

(hereafter, the designation $j \equiv J + 1/2$ is used). The functional form of the asymmetric top rotational energy is different in the E^C subspace ($Cj^2 < E < Bj^2$, a molecule rotates nearly around its axis of the highest moment of inertia) and in the E^A subspace ($Bj^2 < E < Aj^2$, a molecule rotates nearly around its axis of the smallest moment of inertia). Just the same phenomenon takes place for a classical asymmetric top [35]. As has been mentioned above, we chose the axis C of the highest moment of inertia to be the quantization axis. The corresponding semiclassical formulas for the rotational energy are given in Table 1. It must be stressed that these are not exact semiclassical expressions for the rotational energy, but the high j expressions, that are valid with the accuracy $O(1/j)$. It is clear enough that $O(1/j)$ corrections will not contribute significantly to the semiclassical (high j) expressions for rotational frequencies. At least, their contributions will be small for several first transients. That is why the neglecting by the $O(1/j)$ terms is totally justified. One also should keep in mind that the semiclassical values of the rotational energy are doubly degenerate [30–32]. Roughly speaking, the rotational levels belonging to the E^C subspace are doubly degenerate in the clockwise and counterclockwise rotation (this corresponds to the substitution $K \rightarrow -K$ in Eq. (14)), and the rotational levels belonging to the

Table 1
Rotational energies and frequencies for quantum asymmetric tops

$Cj^2 < E < Bj^2$	$Bj^2 < E < Aj^2$
$E(j, N) = Cj^2 + 2j(j \mp N)x_C - (j \mp N)^2 y_C + O(1/j),$ $\quad N = \pm J, \pm(J-1), \pm(J-2)\ldots$	$E(j, N) = Aj^2 - 2j(N+1/2)x_A + (N+1/2)^2 y_A + O(1/j),$ $\quad N = 0, 1, 2\ldots$
$x_C = \sqrt{(A-C)(B-C)}, \quad y_C = (A+B)/2 - C$	$x_A = \sqrt{(A-C)(A-B)}, \quad y_A = A - (C+B)/2$
$\omega_{j,N}^C = 2j\omega_2^C + 2(j-N)\omega_1^C + \Delta^C$	$\omega_{j,N}^A = 2j\omega_2^A + 2(N+1/2)\omega_1^A + \Delta^A$
$\omega_2^C = C\Delta j + x_C(\Delta j - \Delta N)$	$\omega_2^A = A\Delta j - x_A \Delta N$
$\omega_1^C = x_C \Delta j - y_C(\Delta j - \Delta N)$	$\omega_1^A = -x_A \Delta j + y_A \Delta N$
$\Delta^C = C\Delta j^2 + 2x_C \Delta j(\Delta j - \Delta N) - y_C(\Delta j - \Delta N)^2$	$\Delta^A = C\Delta j^2 - 2x_A \Delta j \Delta N + y_A \Delta N^2$

E^A subspace are doubly degenerate for the neighboring odd and even K in Eq. (14). The higher order corrections to the lowest order semiclassical formulas will result in the splitting of the formerly degenerate rotational levels [30–32]. These corrections, being exponentially small, are beyond the accuracy of the semiclassical approximation considered here. Note also that, in the symmetric top limit $A \approx B$, the quantum number N reduces to the standard symmetric top quantum number K.

It is absolutely clear from Eqs. (9) and (13) that the RR frequencies are determined by the expression,

$$\omega_{j,N} = \{E(j + \Delta j, N + \Delta N) - E(j, N)\}/\hbar. \qquad (16)$$

According to the selection rules (10), $|\Delta j| \leqslant \lambda$, but no direct limitations are imposed on ΔN and, generally, all $f_{KN}^J \neq 0$. However, some approximate selection rules on ΔN can still be derived (see below). The explicit values of frequencies (16) in the E^C and E^A subspaces are presented in Table 1. Hereafter, the rotational constants are given in the units of Planck constant h.

4. Results and discussion

By inspecting Eqs. (9), (13), and Table 1, one immediately concludes that the anisotropy of the polarization response is described by the following generic equation:

$$r^\lambda(t) = \sum_{\alpha,\beta=-n}^{n} a_{\alpha\beta}^\lambda \cos\{2\pi t[\Omega_1\alpha + \Omega_2\beta + \Delta]\}. \qquad (17)$$

Here, the fundamental frequencies Ω_1, Ω_2, and the parameter Δ depend upon molecular constants (Table 1), and explicit expressions for the quantities $a_{\alpha\beta}^\lambda$ are immaterial for the subsequent qualitative discussion. Closely following the general

lines of reasoning presented in Ref. [18], one expects the following behavior for the anisotropy. If frequencies Ω_1 and Ω_2, are incommensurable, several partial RRs arise, e.g., for $\alpha = 0$ with frequency Ω_2, for $\beta = 0$ with frequency Ω_1, for $\alpha = \pm\beta$, with frequency $\Omega_1 \pm \Omega_2$, etc. In any case, only $\sim 2n$ terms from the general set of the $\sim 4n^2$ terms contribute to a particular RR. So, the "capacity" of these RRs is very small. If, however, the rotational constants are such that $\Omega_1 \approx 0$ or $\Omega_2 \approx 0$ or $\Omega_1 \approx \Omega_2$, the RRs arise for an arbitrary α and β, and their capacity is of the order of $4n^2$. It is in this latter case that the RRs are presumed to be quite pronounced and manifest themselves in anisotropy (17). The influence of parameter Δ on the form and polarity of RRs is described in detail in Ref. [18]. Note merely that for the problem under consideration here, Δ is either an integer (this results in the sign-constant transients) or a half-integer (this results in the sign-alternating transients).

Now, the strategy for seeking possible types of RRs is totally transparent. One must check whether for some values of rotational constants $A \geqslant B \geqslant C$ and parameters $\Delta j, \Delta N$ one obtains

$$\omega_1^s \approx 0 \quad \text{or} \quad \omega_2^s \approx 0 \qquad (18a)$$

or

$$\omega_1^s \approx \omega_2^s \qquad (18b)$$

$s = C$ or A. It should be emphasized that one should not limit himself to the search of some specific values of parameters $A \geqslant B \geqslant C$ giving rise to Eqs. (18a) or (18b). One should seek for broad enough, generic classes of molecular tops obeying Eqs. (18a) or (18b). The corresponding classes are given in Table 2.

Being equipped with Tables 1 and 2, one must carefully consider various Δj and ΔN for which

Table 2
Expressions for parameters x_i and y_i in several specific cases

Spherical top, $A \approx B \approx C$	$x_i \approx y_i \approx 0$
Oblate top, $A \approx B > C$	$x_C \approx y_C \approx (A+B)/2 - C, \quad x_A \approx 0$
Prolate top, $A > B \approx C$	$x_A \approx y_A \approx A - (B+C)/2, \quad x_C \approx 0$
Planar top, $I_A + I_B \approx I_C, \; C \approx AB/(A+B)$	$x_C \approx C$
Very prolate top, $A \gg B, C$	$x_A \approx y_A \approx A$

requirements (18a) or (18b) hold true. The results of this work are summarized in Tables 3 and 4. It is essential that the RRs in case (18a) are more stable than in case (18b). It is meant the following. Let us assume that, for some particular values of rotational constants, $\omega_2^s = 0$. A slight variation of the rotational constants produces $\omega_1^s \gg \omega_2^s \neq 0$. Such a very small frequency induces a very high period $T \sim 1/\omega_2^s$. In this case, the RRs are still determined by a single frequency ω_1^s, at least for $t < T$. In case (18b), both the frequencies contribute to the transients on an equal footing, and their detuning gives rise to a broadening of the RR signal. So, the condition (18b) produces the effective rotational frequency $\omega \approx \omega_1^s \approx \omega_2^s \approx (\omega_1^s + \omega_2^s)/2$. To emphasize this, we use in Tables 3 and 4 the sign $=$ for defining Ω in situation (18a) and the sign $\approx$ in situation (18b). That is why the

Table 3
Frequencies and transients in the E^C subspace

Transition	Top symmetry	ω_2^C	ω_1^C	$\varDelta^C$	Transients: type, period and polarity
$\Delta N = 0$	General	$\Delta j(C + x_C)$	$\Delta j(x_C - y_C)$	$\Delta j^2(C + 2x_C - y_C)$	
	Oblate $A \approx B > C$, $x_C \approx y_C$, $\boldsymbol{\Omega = C + x_C}$ $\approx (A + B)/2$	$\Delta j \Omega$	≈ 0	$\Delta j^2 \Omega$	J $|\Delta j| = 1$: $T_{\max} = n/2\Omega$ $|\Delta j| = 2$: $T_{\max} = n/2\Omega$, $T_{\min} = (2m + 1)/4\Omega$
$\Delta j = 0$	General	$-\Delta N x_C$	$\Delta N y_C$	$-\Delta N^2 y_C$	
	Oblate $A \approx B > C$, $\boldsymbol{\Omega \approx x_C \approx y_C} \approx$ $(\boldsymbol{x_C + y_C})/2 \approx$ $(A + B)/2 - C$	$-\Delta N \Omega$	$\Delta N \Omega$	$-\Delta N^2 \Omega$	H $|\Delta N| = 1$: $T_{\max} = n/\Omega$, $T_{\min} = (2m + 1)/2\Omega$; K $|\Delta N| = 2$: $T_{\max} = n/4\Omega$
	Prolate $A > B \approx C$, $x_C \approx 0$, $\boldsymbol{\Omega = y_C} \approx$ $(2A - B - C)/4$	≈ 0	$\Delta N \Omega$	$-\Delta N^2 \Omega$	K′ $|\Delta N| = 1$: $T_{\max} = n/2\Omega$; H′ $|\Delta N| = 2$: $T_{\max} = n/2\Omega$, $T_{\min} = (2m + 1)/4\Omega$
$\Delta j = \Delta N$	General	$\Delta j C$	$\Delta j x_C$	$\Delta j^2 C$	
	Prolate $A > B \approx C$, $x_C \approx 0, \boldsymbol{\Omega = C}$	$\Delta j \Omega$	≈ 0	$\Delta j^2 \Omega$	C $|\Delta j| = 1$: $T_{\max} = n/2\Omega$ $|\Delta j| = 2$: $T_{\max} = n/2\Omega$, $T_{\min} = (2m + 1)/4\Omega$
	Planar $\boldsymbol{\Omega \approx C \approx x_C} \approx$ $(\boldsymbol{C + x_C})/2$	$\Delta j \Omega$	$\Delta j \Omega$	$\Delta j^2 \Omega$	P $|\Delta j| = 1$: $T_{\max} = n/\Omega$, $T_{\min} = (2m + 1)/2\Omega$ $|\Delta j| = 2$: $T_{\max} = n/4\Omega$

Table 4
Frequencies and transients in the E^A subspace

Transition	Top symmetry	ω_2^A	ω_1^A	Δ^A	Transients: type, period, and polarity
$\Delta j = \Delta N$	General	$\Delta j(A - x_A)$	$\Delta j(y_A - x_A)$	$\Delta j^2(A - 2x_A + y_A)$	
	Prolate $A > B \approx C$, $x_A \approx y_A$, $\boldsymbol{\Omega = A - x_A}$ $\approx (B + X)/2$	$\Delta j\Omega$	≈ 0	$\Delta j^2\Omega$	J $\|\Delta j\| = 1$: $T_{\max} = n/2\Omega$ $\|\Delta j\| = 2$: $T_{\max} = n/2\Omega$, $T_{\min} = (2m+1)/4\Omega$
$\Delta j = 0$	General	$-\Delta N x_A$	$\Delta N y_A$	$\Delta N^2 y_A$	
	Prolate $A > B \approx C$, $\boldsymbol{\Omega \approx x_A \approx y_A} \approx$ $(\boldsymbol{x_A + y_A})/2 \approx$ $A - (B + C)/2$	$-\Delta N\Omega$	$\Delta N\Omega$	$\Delta N^2\Omega$	H $\|\Delta N\| = 1$: $T_{\max} = n/\Omega$, $T_{\min} = (2m+1)/2\Omega$; K $\|\Delta N\| = 2$: $T_{\max} = n/4\Omega$
	Oblate $A \approx B > C$, $x_A \approx 0$, $\boldsymbol{\Omega = y_A} \approx$ $(A - B - 2C)/4$	≈ 0	$\Delta N\Omega$	$\Delta N^2\Omega$	K' $\|\Delta N\| = 1$: $T_{\max} = n/2\Omega$; H' $\|\Delta N\| = 2$: $T_{\max} = n/2\Omega$; $T_{\min} = (2m+1)/4\Omega$
$\Delta N = 0$	General	$\Delta j A$	$-\Delta j x_A$	$\Delta j^2 A$	
	Oblate $A \approx B > C$, $x_A \approx 0$, $\boldsymbol{\Omega = A}$	$\Delta j\Omega$	≈ 0	$\Delta j^2\Omega$	A $\|\Delta j\| = 1$: $T_{\max} = n/2\Omega$ $\|\Delta j\| = 2$: $T_{\max} = n/2\Omega$, $T_{\min} = (2m+1)/4\Omega$
	Very prolate $\boldsymbol{\Omega \approx A \approx x_A}$	$\Delta j\Omega$	$\Delta j\Omega$	$\Delta j^2\Omega$	V $\|\Delta j\| = 1$: $T_{\max} = n/\Omega$, $T_{\min} = (2m+1)/2\Omega$; $\|\Delta j\| = 2$: $T_{\max} = n/4\Omega$

J- and C-type transients are less severely affected by the variation of rotational constants than their H- and K-type counterparts.

By comparing Tables 3 and 4 with Table 1 of paper [5], one notifies the following major points. The semiclassical approximation allows one to derive "exact" non-perturbative expressions for the periods of the J-, H-, and K-type transients. In Tables 3 and 4, these expressions are marked by the boldface lettering. The expressions were derived for the first time elsewhere [19–21]. The symmetric top based formulas for the quantities are also given in the tables. These simplified formulas are obtained by the substitution of $A(C)$ by $\{A + B\}/2(\{B + C\}/2)$ in the exact prolate (oblate) symmetric top expressions for the J-, H-, and K-type transients [5,15,16]. The secular approximation (12) also gives rise to the same

results. By expanding the "exact" expressions for the effective frequencies near the appropriate symmetric top limit, one gets

$$\Omega^C = (A + B)/2 - \Gamma^c + O\{(A - B)^3\},$$
$$\Omega^A = (B + C)/2 + \Gamma^A + O\{(B - C)^3\} \tag{19}$$

for the J-type transients and

$$\Omega^C = (A + B - 2C - \Gamma^C)/2 + O\{(A - B)^3\},$$
$$\Omega^A = (2A - B - C - \Gamma^A)/2 + O\{(B - C)^3\} \tag{20}$$

for the K- and H-type transients. Here, the corrections

$$\Gamma^C \equiv (A - B)^2/\{8(A - C)\} \geqslant 0,$$
$$\Gamma^A \equiv (B - C)^2/\{8(A - C)\} \geqslant 0. \tag{21}$$

Eq. (19) in conjunction with Eq. (21) confirms the well-established fact that the molecular asymmetry increases the period of the J-type transients for oblate asymmetric tops and decreases that for prolate asymmetric tops [12]. In addition, one recognizes from Eq. (20) that the asymmetry corrections increase the period of the K- and H-type transients, irrespective of the shape of molecular

tops. Note that the corrections, as well as the "exact" expressions for the RR periods given in Tables 3 and 4, are completely determined by the rotational constants and are independent of the temperature. It is of considerable importance to compare the values of the RR periods predicted by the symmetric top like formulas and "exact" semiclassical ones. The results of this procedure are depicted in Fig. 1 for the J-type transients and in Fig. 2 for the K- and H-type transients. It is surprising that the difference between the two approaches is relatively small, even in the case of high enough molecular asymmetry. This fact supports the validity of estimating the periods of the J-, K- and H-type transients by the implementation of the symmetric top like formulas. The difference becomes substantial when the molecule is far beyond the appropriate symmetric top limit, where the implementation of both kinds of formulas is questionable. However, since the accuracy of the RCS in determining rotational constants is high enough (in GHz, a typical error is 1–10 parts per thousand [5]), the use of the "exact" expressions for the RR periods is preferable. For instance, fluorene and fluorene–Ar complex are
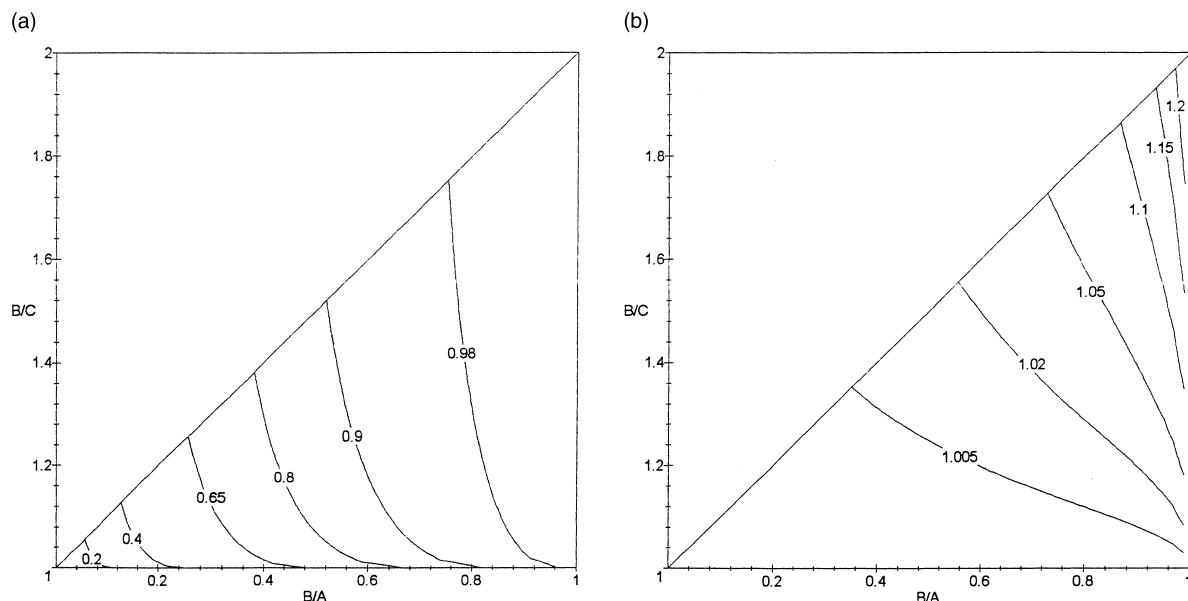

Fig. 1. The ratio of the "exact" and approximate periods of the J-type transients for the (a) E^C subspace and (b) E^A subspace vs. rotational constants.
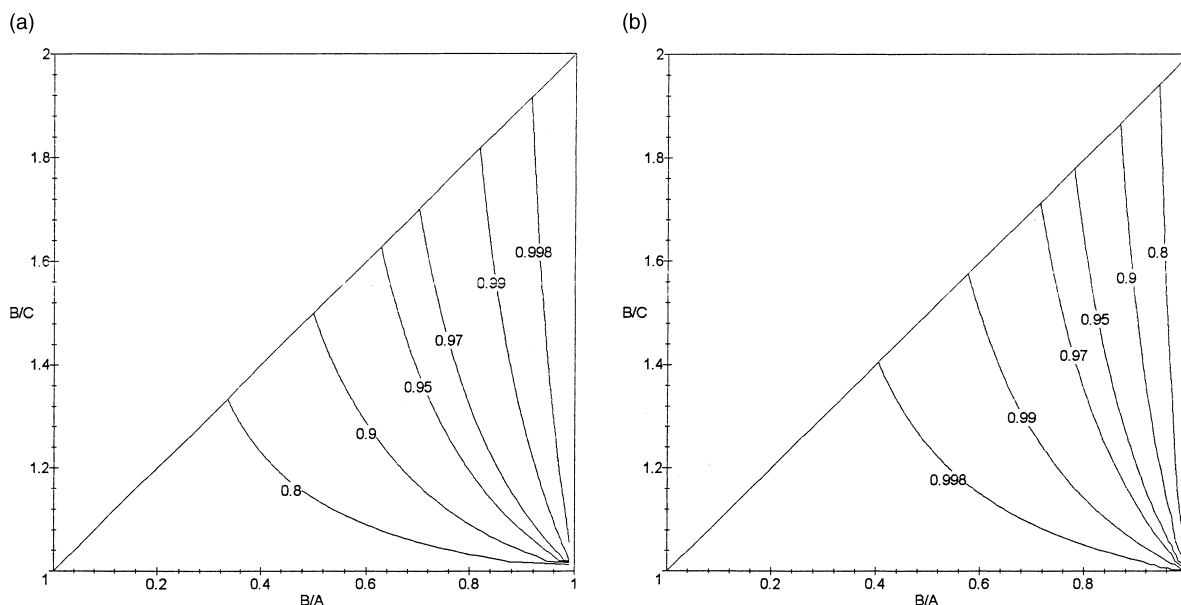
(a)

(b)

Fig. 2. Same as in Fig. 1 but for the H- and K-type transients.

prolate asymmetric tops and exhibit the J-type RRs in the E^A subspace with the period 943.2 ± 3.8 and 1138 ± 3 ps, respectively [16]. The rotational constants for these molecules, obtained by fitting the experimental and simulated RRs, are reported in columns 1–3 of Table 2 of Ref. [16]. By taking these rotational constants, one gets for the periods the following values: 945.9 and 1140.8 ps (symmetric top based formulas), 943.5 and 1137.4 ps (present work, formulas of Table 4). The approach developed in this work gives excellent agreement with experimental results, and the differences between the above two means of calculations of periods, 2.4 and 3.4 ps, are of the order of the accuracy of measurements.

The analyses of Joireman et al. [18] and ours lead to identical predictions for the periods of the C- and A-type transients. It is totally understandable, since both the approaches rely on the semiclassical treatment of the asymmetric top rotation. Note that our consideration also determines the polarity of the C- and A-type transients (Tables 3 and 4).

A remarkable result of the present analyses is the prediction of new types of asymmetric top transients (Tables 3 and 4). The transients labeled as K'- and H'- are similar to the K- and H-type transients.

The origin of the appearance of these new transients can be understood by invoking the following argumentation. As has been mentioned above, the total rotational space of an asymmetric top is subdivided into the E^C and E^A subspaces. If a molecule is nearly an oblate (prolate) symmetric top, the bulk majority of its rotational levels is concentrated in the $E^C (E^A)$ subspace, and the subspace $E^A (E^C)$ has a very small population. It is in this case that the H- and K-type transients occur in the E^C subspace for oblate tops and in the E^A subspace for prolate ones. If a molecule is a prolate or oblate asymmetric top, both E^A and E^C are considerably populated, and the K- and H-type transients take place in both the subspaces. Note however that the polarity of the K-, H- and K'-, H'-type transients is different. For instance, the transition with $|\Delta N| = 1$ in the E^C subspace results in the H- and K' type transients, but that with $|\Delta N| = 2$ results in the K- and H'-type transients. Analogous conclusions are also correct for the E^A subspace.

However, the most important is the prediction of new kinds of transients for planar molecules (Table 3, the P-transients). The point is that the great majority of aromatic species is more or less planar, so that this fact is of considerable

significance for applications. It should be emphasized that the transients obey the same selection rules as the C-ones. In addition, the periods of these transients are nearly those as for the C-type ones. Moreover, if a molecule is rigorously planar $(I_A + I_B = I_C, \ C = AB/(A + B))$ the periods are identically the same $(\Omega = C)$. It is in this case that the C- and P-type transients differ only by their polarity. This observation should be taken into account while interpreting the experimental transients for nearly planar molecules, because the observed C-type transients can actually be the P-type ones and vice versa. Such a misinterpretation will not result in significant errors, since the periods of both the transients are nearly the same, but the polarity of the transients helps one in their correct identifying. In connection with this, it is interesting that aromatic molecules are frequently both prolate and planar. It is the consequence of the present analysis that, if a molecule is planar with a good accuracy and only approximately prolate, the P-type transients will appear instead of the C-type ones. Indeed, if a molecule is strictly planar, than $\omega_1^C = \omega_2^C = C$. So, the requirement $\omega_1^C = C, \ \omega_2^C = 0$, which is necessary for arising the C-type transients, is not obeyed even for highly prolate (but planar) tops. This fact appears to account for the polarity of the observed transients with the period $1/4C$ for planar tops (see e.g., Figs. 3b, c, 5, 6, and 8 of paper [18]). The transients depicted in these figures were identified as the C-type ones, but their sign constant polarity and period, according to Table 3, correspond to the P-type transients with $|\Delta j| = 2$. The molecules that are not planar exhibit the sign alternating transients (see e.g. Fig. 3a of paper [18]). The transients can be identified with the C-type transients corresponding to $|\Delta j| = 2$. If a molecule is prolate but only roughly planar, the C- and P-type transients are in a competition. For $|\Delta j| = 2$, the maxima and minima of the transients at $t = (2n + 1)/4C$ will approximately reconcile each other, so that the maxima at $t = n/2C$ will only survive. This will result in the effective doubling of the RR period. Of course, the above arguments should largely be considered as speculations because a more accurate analysis, based on the rigorous calculation of quantum OCFs, is required.

Also, the V-type transients are predicted for very prolate molecules, for which $A \gg B, C$ (Table 4).

Up to this point, no discussion has been made of the relative intensity of various kinds of transients. A cursory analyses of expression (9) shows that the RR intensities are determined by the values of the pertinent Clebsch–Gordan coefficients (one can use the high j asymptotic expressions for these coefficients [36]), and by the values of eigenfunctions f_{KN}^J which are also calculable semiclassically [28–30]. The inspection of the corresponding formulas allows one to draw the following conclusion. Let the quantum numbers N and j (and therefore rotational energy $E(N, j)$) be fixed. Then, if a molecule rotates nearly around its highest (smallest) moment of inertia, the highest value of f_{KN}^J corresponds to that of $K_{\max}$, for which the difference $|B_j^2 - (B - C)K_{\max}^2 - E(N, j)|$ ($|A_j^2 - (A - C)K_{\max}^2 - E(N, j)|$) is minimal. The further K is from $K_{\max}$, the smaller are f_{KN}^J. For those N corresponding to the minimal and maximal values of the rotational energy, one can roughly state that $f_{K_{\max}N}^J \approx 1$ and $f_{KN}^J \approx 0$ for $K \neq K_{\max}$. In several cases, these observations allow one to figure out some qualitative estimations for the intensities of transients. For instance, one might expect an intense J-type transients in the $E^C(E^A)$ subspace for oblate (prolate) species with the dipole moments directed along the $C(A)$ axis. However, the most reliable and accurate way for determining the intensities is to calculate quantum asymmetric top OCF (9). Of course, one can perform totally semiclassical calculation of this OCF, but the procedure of finding semiclassical eigenvectors f_{KN}^J appears to be more complicated and time consuming than a direct diagonalization of matrices $H_{K_1 K_2}^J$. The comment also pertains to the problem of establishing the "line shapes" for various transients. The advantage of the semiclassical approach stems mainly from its enabling one to arrive at analytical expressions for the periods of the transients and to determine their polarity.

It is to be pointed out that the classification of the RRs is not exhausted by the contents of Tables 3 and 4. These tables appear to contain description of the most intense RRs. However, by considering the transitions obeying different selection rules (i.e. different values of ΔN and Δj),

one can discover some additional transients. In doing so, one should keep in mind that the higher is $|\Delta N|$, the less intense are the transients (for the second rank symmetric top OCFs $|\Delta N_{\max}| = 2$). For instance, Table 3 can be supplemented by the RRs corresponding to $\Delta N = 2, \Delta j = 1$ for planar tops. In this case, $C \approx x_C, \Omega \approx (x_C + y_C)$, $\omega_2^C \approx 0$, $\omega_1^C \approx \Omega, \Delta^C \approx -\Omega$, and $T_{\max} = n/2\Omega$. Table 4 can be supplemented by the transients corresponding to $\Delta N = -\Delta j$ for very prolate tops $(A \gg B, C)$. In this case, $A \approx x_A \approx y_A$, and $\Omega \approx (x_A + y_A) \approx 2A$, $\omega_2^A \approx \omega_1^A \approx \Delta j\Omega$, $\Delta^A \approx 2\Delta j\Omega$. So, for $|\Delta j| = 1$, $T_{\max} = n/2\Omega$ and for $|\Delta j| = 2$, $T_{\max} = n/4\Omega$. These new transients are sign constant. However, the question about the intensity of these, as well as other possible transients, deserves additional investigation.

On concluding this section, it is pertinent to remark that, throughout the article, the axis of the highest moment of inertia is taken as the quantization axis. One arrives at the very similar results by choosing the axis of the smallest moment of inertia to be the quantization axis. In this case, all the results and conclusions, in particular in Tables 3 and 4, remain unchanged. The only difference is that the states with the smallest rotational energy correspond to nearly zero projection of the angular momentum on the quantization axis, and the states with the highest rotational energy correspond to the maximal absolute value of the projection of the angular momentum on the quantization axis [28–30]. If one takes the axis of the intermediate moment of inertia to be the quantization axis, the situation is very different in the sense that there are no states for which the angular momentum is approximately pointed along the quantization axis [28–30]. This directly corresponds to instability of the rotation of a classical asymmetric top around its axis of the intermediate moment of inertia. External perturbations can however stabilize molecular rotation around its intermediate moment of inertia [37].

5. Conclusion

Qualitatively, an asymmetric top undergoes two kinds of precessions, with frequencies that are complicatedly dependent on quantum numbers and rotational constants. To state simply, one expects the onset of the RRs when the two frequencies are collapsed into a single effective frequency, that depends linearly on a quantum number. There are two groups of situations that meet the criterion. First, a molecule can approximately have a higher symmetry (nearly a spherical top, or nearly a linear rotor, or nearly a symmetric top, or nearly a planar top). Second, a molecule can be an asymmetric top, rotating nearly around its axes of the smallest or highest moment of inertia (the axis of the intermediate moment of inertia must be disregarded since rotation around it is unstable). It is in these cases a complicated rotation of an asymmetric top approximately reduces to one-dimensional rotation exhibiting the RRs.

In this paper, the above qualitative expectations are put on reliable mathematical grounds. The semiclassical approach to the description of the asymmetric top rotation is invoked to the analyses of the RRs. This allows us to perform a complete analysis and classification of the RRs for collisionless asymmetric top molecules. More specifically, "exact" non-perturbative expressions are derived for the periods of the J-, H-, and K-type transients. These formulas automatically account for the phenomenon of increasing the period of the J-type transients for oblate asymmetric tops and decreasing that for prolate asymmetric tops in parallel with increase of molecular asymmetry [16]. The asymmetry corrections are demonstrated to magnify the period of the K- and H-type transients, irrespective of the form of molecular top. The polarity of the A- and C-transients is established. New kinds of transients, that are designated as H′, K′, P, and V, are predicted and characterized by their periods and polarity. The most important of these are the P-type transients arising for planar molecules. Our main findings are summarized in Tables 3 and 4, that generalize Table 1 of Ref. [5]. The establishing of new kinds of transients is not only of purely theoretical significance. The point is that a molecule has, in general, three different main moments of inertia. The transients of different types possess, as a rule, different periods. The latter are uniquely determined

by the main moments of inertia. So, one generally requires to measure three different transients for identifying molecular moments of inertia, and the characterization of new kinds of RRs is very helpful in this respect. In conclusion, we note that the semiclassical approach can be applied to the study of the influence of molecular flexibility and external fields on the periods of the RRs. The work on these topics is currently in progress.

Acknowledgements

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